UNITED STATES PATENT AND TRADEMARK OFFICE

I, Susan POTTS BA ACIS,

Director of RWS Group plc, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.

2. That the translator responsible for the attached translation is well acquainted with the French and English languages.

3. That the attached is, to the best of RWS Group plc knowledge and belief, a true translation into the English language of the specification in French filed with the application for a patent in the U.S.A. on July 11, 2001
under the number 09/901679

4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.

For and on behalf of RWS Group plc
The 29th day of August 2001

COMPOSITION BASED ON NANOPARTICLES OR A NANOLATEX OF POLYMERS FOR FABRIC CARE

The present invention relates to a composition for fabric care, in particular for cotton-based fabrics, comprising nanoparticles or a nanolatex of a polymer which is insoluble under the direct and/or indirect working conditions of the said composition in an aqueous or wet medium.

The expression "fabric care" means the protection of fabrics against physical or chemical degradation phenomena and/or the provision of benefits thereto, for instance softening and/or crease-resistance properties.

The machine washing of fabrics leads to a physical and chemical degradation of the fibres and most particularly of cotton fibres. The alkalinity delivered by detergents and also by certain specific compounds such as oxidizing substances (perborate or percarbonate) or certain enzymes may be the cause of the chemical degradation of cotton fibres. However, it is generally the combination of the chemical and mechanical actions which leads to degradation of the fibres. The mechanical action is produced during the washing, rinsing, spin-drying or tumble-drying, when the latter takes place in a tumble dryer. This degradation of the fibres leads to the formation of

fibrils at the surface of the textile which end up causing coloured textiles to lose their radiance. This degradation also induces a decrease in the strength of the textile which, at the extreme, may lead to tearing of the fabrics. This degradation of textiles may be evaluated quantitatively either by a loss of the colours of coloured textiles or by a reduction in the tear strength of the textile. It is generally necessary to carry out 10 to 20 cumulative machine washes in order to perceive this type of degradation.

Cleaning in a washing machine, which systematically includes a spin-drying operation, also leads to creased fabrics, which is accentuated during the tumble-drying stage, in particular by the formation of inter-fibre hydrogen bonds. It is thus necessary to iron the fabrics in order to make them look presentable.

In order to reduce the degradation of the fibres during washing or rinsing, the suppliers of chemical products or detergents have made use of changes in detergent formulations or have used certain specific additives.

Mention may be made in particular of detergents comprising no oxidizing system, but which have reduced cleaning capacities.

Silicone-based compounds have also been used, and in particular aminosilicones (US-A-4 585 563; WO 92/07927; WO 98/39401).

The Applicant has found that the use, in compositions for treating fabrics, in particular cotton-based fabrics, of nanoparticles or of a nanolatex of insoluble polymers makes it possible to prevent the degradation of the fabrics and/or to give them crease-resistance and/or softening properties.

Such compositions may especially be compositions for washing and/or rinsing and/or softening fabrics, for destaining fabrics before washing ("prespotting"), for tumble-drying wet fabrics in a tumble dryer or for ironing fabrics.

According to the invention, the expression "polymer nanoparticles" means particles with a diameter from about 10 to 500 nm, preferably from 20 to 300 nm, most particularly from 20 to 100 nm and even more particularly from 20 to 50 nm.

The expression "polymer nanolatex" means a stable aqueous dispersion of solid polymer nanoparticles with a mean size from about 10 to 500 nm, preferably from 20 to 300 nm, most particularly from 20 to 100 nm and even more particularly from 20 to 50 nm. Such a dispersion generally has a solids content from about 10% to 50% by weight and preferably from about 20% to 40% by weight.

A first subject of the invention consists of a composition for fabric care, characterized in that it comprises nanoparticles or at least one nanolatex of at least one polymer (P) which is insoluble under the working conditions of the said composition in an aqueous or wet medium.

A second subject of the invention consists of a process for fabric care by treating these fabrics with a composition, in an aqueous or wet medium, comprising nanoparticles or at least one nanolatex of at least one polymer (P) which is insoluble in the said medium.

A third subject of the invention consists of the use, in a composition for treating fabrics in an aqueous or wet medium, of nanoparticles or of at least one nanolatex of at least one polymer (P) which is insoluble in the said medium, as an agent for fabric care.

The composition and the working (or treatment) conditions may be in numerous forms.

The said composition may be

* in the form of a solid (powder, granules, tablets, etc.) or of a concentrated aqueous dispersion, placed in contact with the fabrics to be treated, after dilution in water;

* in the form of a concentrated dispersion placed beforehand on the dry fabrics to be treated before dilution in water;

* in the form of an aqueous dispersion to be placed directly on the dry fabrics to be treated without dilution or of a solid support (stick) comprising the said nanoparticles or the said nanolatex, to be applied directly to the dry fabrics to be treated;

* in the form of an insoluble solid support comprising the said nanoparticles or the said nanolatex of polymer (P) placed directly in contact with the wet fabrics to be treated.

Thus, the composition of the invention may be:

- a solid or liquid detergent formulation capable of directly forming a washing bath by dilution;
- a liquid rinsing and/or softening formulation capable of directly forming a rinsing and/or softening bath by dilution;
- a solid material, in particular a textile, comprising the said nanoparticles or the said nanolatex, which is intended to be placed in contact with wet fabrics in a tumble dryer (the said solid material is referred to hereinbelow as a "tumble dryer additive");
- an aqueous ironing formulation;

- a washing additive ("prespotter") intended to be placed on the dry fabrics prior to a washing operation using a detergent formulation containing or not containing the said nanoparticles or the said nanolatex (the said additive is referred to hereinbelow as a "prespotter").

The composition of the invention is particularly suitable for fabric care, especially for cotton-based fabrics, in particular fabrics containing at least 35% cotton.

The said polymer (P) preferably has a glass transition temperature Tg from about -40°C to 150°C, preferably from about 0 to 100°C and most particularly from about 10 to 80°C.

The term "polymer" means either a homopolymer or a copolymer derived from two or more monomers.

For good implementation of the invention, the said polymer (P) comprises:

- hydrophobic monomer units (N) that are uncharged or non-ionizable at the working pH of the composition of the invention,
- optionally at least one hydrophilic monomer unit (F) chosen from monomer units
  * (F1) that are cationic or cationizable at the working pH of the said composition,
  * (F2) that are amphoteric at the working pH of the said composition,

* (F3) that are anionic or anionizable at the working pH of the said composition,

* (F4) that are uncharged or non-ionizable, of hydrophilic nature, at the working pH of the said composition,

* or mixtures thereof

- and optionally at least one crosslinking unit (R).

The said monomer units (N) and (F) are preferably derived from α-β monoethylenically unsaturated monomers.

The said monomer units (R) are preferably derived from diethylenically unsaturated monomers.

The average molar mass of the said polymer (measured by gel permeation chromatography (GPC) THF and expressed as polystyrene equivalents) may preferably be at least 20 000.

As examples of monomers from which the hydrophobic units (N) are derived, mention may be made of:

- vinylaromatic monomers such as styrene, vinyltoluene, etc.,
- alkyl esters of α-β monoethylenically unsaturated acids such as methyl, ethyl, etc. acrylates and methacrylates,
- vinyl or allylic esters of saturated carboxylic acids, such as vinyl or allyl acetates, propionates or versatates,

- α-β monoethylenically unsaturated nitriles, such as acrylonitrile, etc.

As examples of monomers from which the cationic or cationizable hydrophilic units (F1) are derived, mention may be made of:

- N,N-(dialkylamino-ω-alkyl)amides of α-β monoethylenically unsaturated carboxylic acids such as N,N-dimethylaminomethyl acrylamide or methacrylamide, N,N-dimethylaminoethyl acrylamide or methacrylamide, N,N-dimethylamino-3-propyl acrylamide or methacrylamide and N,N-dimethylaminobutyl acrylamide or methacrylamide,
- α-β monoethylenically unsaturated amino esters, such as dimethylaminoethyl methacrylate (DMAM), dimethylaminopropyl methacrylate, di-tert-butylaminoethyl methacrylate or dipentylaminoethyl methacrylate,
- monomers that are precursors of amine functions, such as N-vinylformamide, N-vinylacetamide, etc., which generate primary amine functions by simple acidic or basic hydrolysis.

As examples of monomers from which the amphoteric hydrophilic units (F2) are derived, mention may be made of:

- N,N-dimethyl-N-methacryloyloxyethyl-N-(3-sulphopropyl)ammonium sulphobetaine (SPE from Raschig), N,N-dimethyl-N-(2-methacrylamidoethyl)-N-(3-sulphopropyl)ammonium betaine (SPP from Raschig), 1-vinyl-

3-(3-sulphopropyl)imidazolidium betaine or 1-(3-sulphopropyl)-2-vinylpyridinium betaine (SPV from Raschig),

- derivatives of the quaternization reaction of N-(dialkylamino-ω-alkyl)amides of α-β ethylenically unsaturated carboxylic acids, such as N,N-dimethylaminomethyl acrylamide or methacrylamide, N,N-dimethylamino-3-propyl acrylamide or methacrylamide, or ethylenically unsaturated amino esters, such as di-tert-butylaminoethyl methacrylate or dipentylaminoethyl methacrylate, with a chloroacetate of an alkali metal (in particular sodium) or of propane sultone.

As examples of monomers from which the anionic or anionizable hydrophilic units (F3) are derived, mention may be made of:

- monomers containing at least one carboxylic function, such as α-β ethylenically unsaturated carboxylic acids or anhydrides, acrylic, methacrylic, maleic, fumaric or itaconic acids or anhydrides, N-methacroylalanine or N-acryloylhydroxyglycine, and water-soluble salts thereof,
- monomers containing at least one sulphate or sulphonate function, such as 2-sulphooxyethyl methacrylate, vinylbenzenesulphonic acid, allylsulphonic acid, 2-acrylamido-2-methylpropanesulphonic acid, sulphoethyl acrylate or methacrylate, or

sulphopropyl acrylate or methacrylate, and water-soluble salts thereof,

- monomers containing at least one phosphonate or phosphate function, such as vinylphosphonic acid, esters of ethylenically unsaturated phosphates such as phosphates derived from hydroxyethyl methacrylate (Empicryl 6835 from Rhodia) and those derived from polyoxyalkylene methacrylates and water-soluble salts thereof,
- α-β monoethylenically unsaturated monomers that are precursors of anionic function(s), such as those whose hydrolysis generates carboxylate functions (tert-butyl acrylate, dimethylaminoethyl acrylate, maleic anhydride, etc.).

As examples of monomers from which the uncharged or non-ionizable hydrophilic units (F4) are derived, mention may be made of:

- hydroxyalkyl esters of α-β ethylenically unsaturated acids, such as hydroxyethyl, hydroxypropyl, etc. acrylates and methacrylates,
- α-β ethylenically unsaturated acid amides, such as acrylamide, N,N-dimethyl methacrylamide, N-methylol-acrylamide, etc.,
- α-β ethylenically unsaturated monomers bearing a water-soluble polyoxyalkylenated segment of the polyethylene oxide type, such as polyethylene oxide α-methacrylates (Bisomer S20W, S10W, etc. from

Laporte) or α,ω-dimethacrylates, Sipomer BEM from Rhodia (polyoxyethylene ω-behenyl methacrylate), Sipomer SEM-25 from Rhodia (polyoxyethylene ω-tristyrylphenyl methacrylate), etc.,

- α-β ethylenically unsaturated monomers that are precursors of hydrophilic units or segments, such as vinyl acetate, which, once polymerized, may be hydrolysed to generate vinyl alcohol units or polyvinyl alcohol segments,
- α-β ethylenically unsaturated monomers of ureido type and in particular methacrylamidoethyl-2-imidazolidinone (Sipomer WAM II from Rhodia).

As examples of monomers from which the crosslinking units (R) are derived, mention may be made of:

- divinylbenzene
- ethylene glycol dimethacrylate
- allyl methacrylate
- methylenebis(acrylamide)
- glyoxal bis(acrylamide).

The said polymers (P) may be obtained in a known manner by free-radical polymerization in aqueous medium of ethylenically unsaturated monomers. The said nanolatices may be obtained in particular by free-radical emulsion polymerization in water.

Processes for obtaining nanoparticulate latices of small diameter are described in Colloid

Polym. Sci. 266:462-469 (1988) and in Journal of Colloid and Interface Science. Vol. 89, No. 1, September 1982, pages 185 et seq. One method for preparing latices of particles with a mean size of less than 100 nm, in particular with a mean size ranging from 1 to 60 nm and most particularly from 5 to 40 nm, is described in EP-A-644 205.

The choice and relative amounts of the monomer(s) from which the unit(s) (N), (F) and (R) of the polymer (P) are derived are such that the said polymer (P) has a glass transition temperature Tg from about -40°C to 150°C, preferably from about 0 to 100°C and most particularly from about 10 to 80°C, and remains insoluble under the working conditions of the composition of the invention.

According to the invention, the said polymer (P) is considered as insoluble when less than 15% and preferably less than 10% of its weight is soluble in the aqueous or wet working medium of the composition of the invention, that is to say in particular under the temperature and pH conditions of the said medium.

The working pH for the composition of the invention may range from about 2 to about 12, depending on the desired use.

When it is

- a detergent formulation, the pH of the washing bath is generally from about 7 to 11 and preferably from 8 to 10.5;
- a rinsing and/or softening formulation, the pH of the rinsing and/or softening bath is generally from about 2 to 8;
- a tumble dryer additive, the pH to be considered is that of the residual water, which may be from about 2 to 9;
- an aqueous ironing formulation, the pH of the said formulation is generally from about 5 to 9;
- a prespotter, the pH to be considered is that of the washing bath for the operation following the washing, namely from about 7 to 11 and preferably from 8 to 10.5.

For good implementation of the invention, at least 70% of the total mass of the said polymer (P) is formed from hydrophobic unit(s) (N).

When hydrophilic units (F) are present, they preferably represent not more than 30% of the total mass of the polymer (P).

When crosslinking units (R) are present, they generally represent not more than 20%, preferably not more than 10% and most particularly not more than 5% of the total mass of the polymer (P).

A first embodiment of the invention consists of a composition (C1) comprising nanoparticles or at

least one nanolatex of at least one uncharged or non-ionizable polymer (P1) comprising

- at least 70% of its weight of hydrophobic monomer units (N)
- optionally at least 1% of its weight of uncharged or non-ionizable hydrophilic monomer units (F4)
- optionally not more than 20% of its weight of uncharged or non-ionizable crosslinking units (R).

Preferably, according to this first embodiment, the said uncharged or non-ionizable polymer (P1) comprises:

- at least 70% of its weight of hydrophobic monomer units (N)
- from 3% to 30% of its weight of uncharged or non-ionizable hydrophilic monomer units (F4)
- optionally not more than 20% and preferably not more than 10% of its weight of uncharged or non-ionizable crosslinking units (R).

The said uncharged or non-ionizable polymer (P1) may be used in any type of fabric care composition mentioned above, the working pH of which may range from 2 to 12, namely detergent formulations, rinsing and/or softening formulations, tumble dryer additives, aqueous ironing formulations or prespotters.

A second embodiment of the invention consists of a composition (C2) comprising nanoparticles or at least one nanolatex of at least one polymer (P2)

containing anionic or anionizable units and being free of cationic or cationizable units, comprising

- at least 70% of its weight of hydrophobic monomer units (N)
- at least 1% of its weight, preferably from 3% to 30% of its weight and most particularly from 1% to 20% of its weight, of anionic or anionizable hydrophilic monomer units (F3)
- optionally not more than 29% of its weight of uncharged or non-ionizable hydrophilic monomer units (F4).

The said polymer (P2) can be used in fabric care compositions of non-cationic nature, namely detergent formulations, tumble dryer additives, aqueous ironing formulations or prespotters.

A third embodiment of the invention consists of a composition (C3) comprising nanoparticles or at least one nanolatex of at least one polymer (P3) containing amphoteric units, comprising

- at least 70% of its weight of hydrophobic monomer units (N)
- at least 0.1% of its weight, preferably not more than 20% of its weight and most particularly not more than 10% of its weight, of amphoteric hydrophilic monomer units (F2)
- optionally uncharged or non-ionizable hydrophilic monomer units (F4)

- optionally cationic or cationizable hydrophilic monomer units (F1),

the combination of hydrophilic monomer units (F) preferably representing at least 1% of the weight of the polymer (P3), and the molar ratio of the cationic charges to the anionic charges possibly ranging from 1/99 to 80/20 depending on the desired use of the said composition (C3).

The said polymer (P3) with a molar ratio of the cationic charges to the anionic charges ranging from 1/99 to 80/20 may be used in tumble dryer additives and aqueous ironing formulations.

The said polymer (P3) with a molar ratio of the cationic charges to the anionic charges ranging from 1/99 to 60/40 and preferably from 5/95 to 50/50 may also be used in detergent formulations and prespotters.

A fourth embodiment of the invention consists of a composition (C4) comprising nanoparticles or at least one nanolatex of at least one polymer (P4) containing both cationic or cationizable units and anionic or anionizable units, comprising

- at least 70% of its weight of hydrophobic monomer units (N)
- cationic or cationizable hydrophilic monomer units (F1)
- anionic or anionizable hydrophilic monomer units (F3)

- optionally amphoteric hydrophilic monomer units (F2)
- optionally uncharged or non-ionizable hydrophilic monomer units (F4),

the combination of hydrophilic monomer units (F) preferably representing at least 1% of the weight of the polymer (P4), and the molar ratio of the cationic charges to the anionic charges possibly ranging from 1/99 to 80/20 depending on the desired use of the said composition (C4).

The said polymer (P4) with a molar ratio of the cationic charges to the anionic charges ranging from 1/99 to 80/20 may be used in tumble dryer additives and aqueous ironing formulations.

The said polymer (P4) with a molar ratio of the cationic charges to the anionic charges ranging from 1/99 to 60/40 and preferably from 5/95 to 50/50 may also be used in detergent formulations and prespotters.

A fifth embodiment of the invention consists of a composition (C5) comprising nanoparticles or at least one nanolatex of at least one polymer (P5) containing cationic or cationizable units and being free of anionic or anionizable units, comprising

- at least 70% of its weight of hydrophobic monomer units (N)
- at least 1% of its weight, preferably from 3% to 30% of its weight and most particularly from 1% to 10% of

its weight, of cationic or cationizable hydrophilic monomer units (F1)

- optionally not more than 20% of its weight of uncharged or non-ionizable hydrophilic monomer units (F4).

The said polymer (P5) may be used in any type of fabric care composition mentioned above, the working pH of which may range from 2 to 12, namely detergent formulations, rinsing and/or softening formulations, tumble dryer additives, aqueous ironing formulations or prespotters.

In a most preferred manner, when the composition (C5) is a detergent composition, the said monomer units (F1) are cationizable units derived from at least one cationizable monomer with a pKa of less than 11 and preferably of less than 10.5.

As examples of nanoparticles or a nanolatex of polymer (P), mention may be made in particular of nanoparticles or a nanolatex of copolymers containing units derived from

* methyl methacrylate/butyl acrylate/hydroxyethyl methacrylate/methacrylic acid, the glass transition temperature Tg of which may range from 10°C to 80°C, depending on the composition of the said polymer
* methyl methacrylate/ethylene glycol dimethacrylate/ methacrylic acid, the glass transition temperature Tg

of which may range from 10°C to 80°C, depending on the composition of the said polymer

* styrene/divinylbenzene/methacrylic acid, the glass transition temperature Tg of which may range from 100°C to 140°C, depending on the composition of the said polymer

* styrene/butyl acrylate/hydroxyethyl methacrylate/methacrylic acid, the glass transition temperature Tg of which may range from 10°C to 80°C, depending on the composition of the said polymer

* Veova 10 (vinyl C_{10} versatate)/methyl methacrylate/butyl acrylate/methacrylic acid, the glass transition temperature Tg of which may range from 10°C to 80°C, depending on the composition of the said polymer

* methyl methacrylate/butyl acrylate/hydroxyethyl methacrylate/methacrylic acid/N,N-dimethyl-N-methacryloyloxyethyl-N-(3-sulphopropyl)ammonium sulphobetaine (SPE from Raschig), the glass transition temperature Tg of which may range from 10°C to 80°C, depending on the composition of the said polymer

* methyl methacrylate/butyl acrylate/hydroxyethyl methacrylate/methacrylic acid/vinylphosphonic acid, the glass transition temperature Tg of which may range from 10°C to 80°C, depending on the composition of the said polymer

* methyl methacrylate/butyl acrylate/hydroxyethyl methacrylate/methacrylic acid/Empicryl 6835 from

Rhodia, the glass transition temperature Tg of which may range from 10°C to 80°C, depending on the composition of the said polymer.

The amount of nanoparticles or of nanolatex of polymer (P) present in the care composition according to the invention may range from 0.05% to 10% as dry weight relative to the dry weight of the said composition, depending on the desired application.

Thus, the said polymer (P) may be used as follows:

% of nanoparticles or nanolatex of polymer (P) (as dry weight)	In a care composition according to the invention used as
0.05 - 5 preferably 0.1 - 3	detergent formulation
0.05 - 3 preferably 0.1 - 2	rinsing and/or softening formulation
0.05 - 10 preferably 0.1 - 5	tumble dryer additive
0.05 - 10 preferably 0.1 - 5	ironing formulation
0.05 - 10 preferably 0.1 - 5	prespotter

Other constituents may be present, along with the nanoparticles or the nanolatex of polymer (P), in the care composition according to the invention. The nature of these constituents depends on the desired use of the said composition.

Thus, when it is a detergent formulation, for washing fabrics, it generally comprises:

- at least one natural and/or synthetic surfactant,
- at least one detergent adjuvant ("builder")
- optionally an oxidizing agent or system, and
- a series of specific additives.

The detergent formulation may comprise surfactants in an amount corresponding to about 3% to 40% by weight relative to the detergent formulation, these surfactants being such as

Anionic surfactants

· alkyl ester sulphonates of formula $R-CH(SO_3M)-COOR'$, in which R represents a C_8-C_{20} and preferably C_{10}-C_{16} alkyl radical, R' represents a C_1-C_6 and preferably C_1-C_3 alkyl radical and M represents an alkali metal (sodium, potassium or lithium) cation, a substituted or unsubstituted ammonium (methyl-, dimethyl-, trimethyl- or tetramethylammonium, dimethylpiperidinium, etc.) or an alkanolamine derivative (monoethanolamine, diethanolamine, triethanolamine, etc.). Mention may be made most particularly of methyl ester sulphonates in which the radical R is C_{14}-C_{16};

· alkyl sulphates of formula $ROSO_3M$, in which R represents a C_5-C_{24} and preferably C_{10}-C_{18} alkyl or hydroxyalkyl radical, M representing a hydrogen atom or a cation of the same definition as above, and also the

ethoxylenated (EO) and/or propoxylenated (PO) derivatives thereof, containing on average from 0.5 to 30 and preferably from 0.5 to 10 EO and/or PO units;

· alkylamide sulphates of formula $RCONHR'OSO_3M$ in which R represents a C_2-C_{22} and preferably C_6-C_{20} alkyl radical, R' represents a C_2-C_3 alkyl radical, M representing a hydrogen atom or a cation of the same definition as above, and also the ethoxylenated (EO) and/or propoxylenated (PO) derivatives thereof, containing on average from 0.5 to 60 EO and/or PO units;

· saturated or unsaturated C_8-C_{24} and preferably C_{14}-C_{20} fatty acid salts, C_9-C_{20} alkylbenzenesulphonates, primary or secondary C_8-C_{22} alkylsulphonates, alkylglyceryl sulphonates, the sulphonated polycarboxylic acids described in GB-A-1 082 179, paraffin sulphonates, N-acyl N-alkyltaurates, alkyl phosphates, isethionates, alkyl succinamates, alkyl sulphosuccinates, sulphosuccinate monoesters or diesters, N-acyl sarcosinates, alkylglycoside sulphates, polyethoxycarboxylates; the cation being an alkali metal (sodium, potassium or lithium), a substituted or unsubstituted ammonium residue (methyl-, dimethyl-, trimethyl- or tetramethylammonium, dimethylpiperidinium, etc.) or an alkanolamine derivative (monoethanolamine, diethanolamine, triethanolamine, etc.);

Nonionic surfactants

· polyoxyalkylenated (polyoxyethylenated, polyoxypropylenated or polyoxybutylenated) alkylphenols in which the alkyl substituent is C_6-C_{12} and containing from 5 to 25 oxyalkylene units; examples which may be mentioned are the products Triton X-45, X-114, X-100 or X-102 sold by Rohm & Haas Co.;

· glucosamide, glucamide or glycerolamide;

· polyoxyalkylenated C_8-C_{22} aliphatic alcohols containing from 1 to 25 oxyalkylene (oxyethylene or oxypropylene) units; examples which may be mentioned are the products Tergitol 15-S-9 and Tergitol 24-L-6 NMW sold by Union Carbide Corp., Neodol 45-9, Neodol 23-65, Neodol 45-7 and Neodol 45-4 sold by Shell Chemical Co., and Kyro EOB sold by The Procter & Gamble Co.;

· products resulting from the condensation of ethylene oxide or the compound resulting from the condensation of propylene oxide with propylene glycol, such as the Pluronic products sold by BASF;

· products resulting from the condensation of ethylene oxide or the compound resulting from the condensation of propylene oxide with ethylenediamine, such as the Tetronic products sold by BASF;

· amine oxides such as C_{10}-C_{18} alkyl dimethylamine oxides and C_8-C_{22} alkoxy ethyl dihydroxyethylamine oxides;

· the alkylpolyglycosides described in US-A-4 565 647;

· C_8-C_{20} fatty acid amides;

· ethoxylated fatty acids;

· ethoxylated fatty amides;

· ethoxylated amines.

Amphoteric and zwitterionic surfactants

· alkyldimethylbetaines, alkylamidopropyldimethylbetaines, alkyltrimethylsulphobetaines and the products of condensation of fatty acids and of protein hydrolysates;

· alkyl amphoacetates or alkyl amphodiacetates in which the alkyl group contains from 6 to 20 carbon atoms.

The detergent adjuvants ("builders") for improving the surfactant properties may be used in amounts corresponding to about 5-50% and preferably to about 5-30% by weight for the liquid detergent formulations or to about 10-80% and preferably 15-50% by weight for the powder detergent formulations, these detergent adjuvants being such as:

Mineral detergent adjuvants

· polyphosphates (tripolyphosphates, pyrophosphates, orthophosphates or hexametaphosphates) of alkali metals, of ammonium or of alkanolamines

· tetraborates or borate precursors;

· silicates, in particular those with an SiO_2/Na_2O ratio from about 1.6/1 to 3.2/1 and the lamellar silicates described in US-A-4 664 839;

· alkali metal or alkaline-earth metal carbonates (bicarbonates, sesquicarbonates);

· cogranulates of alkali metal silicate hydrates and of alkali metal (sodium or potassium) carbonates that are rich in silicon atoms in Q2 or Q3 form, described in EP-A-488 868;

· crystalline or amorphous aluminosilicates of alkali metals (sodium or potassium) or of ammonium, such as zeolites A, P, X, etc.; zeolite A with a particle size of about 0.1-10 micrometers is preferred.

Organic detergent adjuvants

· water-soluble polyphosphonates (ethane 1-hydroxy-1,1-diphosphonates, methylenediphosphonate salts, etc.);

· water-soluble salts of carboxylic polymers or copolymers or water-soluble salts thereof, such as:

- polycarboxylate ethers (oxydisuccinic acid and its salts, monosuccinic acid tartrate and its salts, disuccinic acid tartrate and its salts);
- hydroxypolycarboxylate ethers;
- citric acid and its salts, mellitic acid and succinic acid and their salts;
- polyacetic acid salts (ethylenediaminetetraacetates, nitrilotriacetates, N-(2-hydroxyethyl)nitrilodiacetates);
- C_5-C_{20} alkyl succinic acids and their salts (2-dodecenyl-succinates, lauryl succinates);
- carboxylic polyacetal esters;
- polyaspartic acid and polyglutamic acid and their salts;

- polyimides derived from the polycondensation of aspartic acid and/or of glutamic acid;
- polycarboxymethyl derivatives of glutamic acid or of other amino acids.

The detergent formulation may also comprise at least one oxygen-releasing bleaching agent comprising a percompound, preferably a persalt.

The said bleaching agent may be present in an amount corresponding to about 1% to 30% and preferably from 4% to 20% by weight relative to the detergent formulation.

As examples of percompounds which may be used as bleaching agents, mention should be made in particular of perborates such as sodium perborate monohydrate or tetrahydrate; peroxygenated compounds such as sodium carbonate peroxyhydrate, pyrophosphate peroxyhydrate, urea peroxyhydrate, sodium peroxide and sodium persulphate.

The preferred bleaching agents are sodium perborate monohydrate or tetrahydrate and/or sodium carbonate peroxyhydrate.

The said agents are generally combined with a bleaching activator which generates, in situ in the washing medium, a peroxycarboxylic acid in an amount corresponding to about 0.1% to 12% and preferably from 0.5% to 8% by weight relative to the detergent formulation. Among these activators, mention may be

made of tetraacetylethylenediamine, tetraacetylmethylenediamine, tetraacetylglycoluryl, sodium p-acetoxybenzenesulphonate, pentaacetylglucose and octaacetyllactose.

Mention may also be made of non-oxygenated bleaching agents, which act by photo-activation in the presence of oxygen, these being agents such as sulphonated aluminium and/or zinc phthalocyanins.

The detergent formulation may also comprise soil-release agents, anti-redeposition agents, chelating agents, dispersants, fluorescers, foam suppressants, softeners, enzymes and various other additives.

Soil-release agents

These may be used in amounts of about 0.01-10%, preferably about 0.1-5% and more preferably about 0.2-3% by weight.

Mention may be made more particularly of agents such as:

· cellulose derivatives such as cellulose hydroxy ethers, methylcellulose, ethylcellulose, hydroxypropylmethylcellulose or hydroxybutylmethylcellulose;

· polyvinyl esters grafted onto polyalkylene trunks, such as polyvinyl acetates grafted onto polyoxyethylene trunks (EP-A-219 048);

· polyvinyl alcohols;

· polyester copolymers based on ethylene terephthalate and/or propylene terephthalate and polyoxyethylene terephthalate units, with an ethylene terephthalate and/or propylene terephthalate (number of units)/ polyoxyethylene terephthalate (number of units) molar ratio from about 1/10 to 10/1 and preferably from about 1/1 to 9/1, the polyoxyethylene terephthalates containing polyoxyethylene units with a molecular weight from about 300 to 5 000 and preferably from about 600 to 5 000 (US-A-3 959 230, US-A-3 893 929, US-A-4 116 896, US-A-4 702 857, US-A-4 770 666);

· sulphonated polyester oligomers obtained by sulphonation of an oligomer derived from ethoxylated allylic alcohol, from dimethyl terephthalate and from 1,2-propylene diol, containing from 1 to 4 sulphonated groups (US-A-4 968 451);

· polyester copolymers based on propylene terephthalate and polyoxyethylene terephthalate units and ending with ethyl or methyl units (US-A-4 711 730) or polyester oligomers ending with alkylpolyethoxy groups (US-A-4 702 857) or sulphopolyethoxy (US-A-4 721 580) or sulphoaroyl (US-A-4 877 896) anionic groups;

· sulphonated polyester copolymers derived from terephthalic, isophthalic and sulphoisophthalic acid, anhydride or diester and from a diol (FR-A-2 720 399).

Anti-redeposition agents

These may be used in amounts generally of about 0.01-10% by weight for a powder detergent formulation or about 0.01-5% by weight for a liquid detergent formulation.

Mention may be made in particular of agents such as:

- ethoxylated monoamines or polyamines, and ethoxylated amine polymers (US-A-4 597 898, EP-A-11 984);
- carboxymethylcellulose;
- sulphonated polyester oligomers obtained by condensation of isophthalic acid, dimethyl sulphosuccinate and diethylene glycol (FR-A-2 236 926);
- polyvinylpyrrolidones.

Chelating agents

Agents for chelating iron and magnesium may be present in amounts of about 0.1-10% and preferably of about 0.1-3% by weight.

Mention may be made, inter alia, of:

- aminocarboxylates such as ethylenediaminetetraacetates, hydroxyethylethylenediaminetriacetates and nitrilotriacetates;
- aminophosphonates such as nitrilotris(methylenephosphonates);
- polyfunctional aromatic compounds such as dihydroxydisulphobenzenes.

Polymeric dispersants

These may be present in an amount of about 0.1-7% by weight, to control the calcium and magnesium hardness, these being agents such as:

· water-soluble polycarboxylic acid salts with a molecular mass from about 2 000 to 100 000, obtained by polymerization or copolymerization of ethylenically unsaturated carboxylic acids such as acrylic acid, maleic acid or anhydride, fumaric acid, itaconic acid, aconitic acid, mesaconic acid, citraconic acid or methylenemalonic acid, and most particularly polyacrylates with a molecular mass from about 2 000 to 10 000 (US-A-3 308 067), copolymers of arylic acid and of maleic anhydride with a molecular mass from about 5 000 to 75 000 (EP-A-66 915);

· polyethylene glycols with a molecular mass from about 1 000 to 50 000.

Fluorescers (brighteners)

These may be present in an amount of about 0.05-1.2% by weight, these being agents such as: stilbene, pyrazoline, coumarin, fumaric acid, cinnamic acid, azole, methinecyanin, thiophene, etc. derivatives ("The production and application of fluorescent brightening agents" - M. Zahradnik, published by John Wiley & Sons, New York, 1982).

Foam suppressants

These may be present in amounts which may be up to 5% by weight, these being agents such as:

· C_{10}-C_{24} monocarboxylic fatty acids or alkali metal, ammonium or alkanolamine salts thereof, and fatty acid triglycerides;

· saturated or unsaturated aliphatic, alicyclic, aromatic or heterocyclic hydrocarbons, such as paraffins and waxes;

· N-alkylaminotriazines;

· monostearyl phosphates and monostearyl alkyl phosphates;

· polyorganosiloxane oils or resins optionally combined with silica particles.

Softeners

These may be present in amounts of about 0.5-10% by weight, these being agents such as clays.

Enzymes

These may be present in an amount which may be up to 5 mg by weight and preferably of about 0.05-3 mg of active enzyme/g of detergent formulation, these being enzymes such as:

· proteases, amylases, lipases, cellulases and peroxidases (US-A-3 553 139, US-A-4 101 457, US-A-4 507 219, US-A-4 261 868).

Other additives

Mention may be made, inter alia, of:

- buffers,
- fragrances,
- pigments.

The detergent formulation may be used, in particular in a washing machine, in a proportion of from 0.5 g/l to 20 g/l and preferably from 2 g/l to 10 g/l to carry out washing operations at a temperature from about 25 to 90°C.

A second embodiment of the care composition of the invention consists of an aqueous liquid formulation for rinsing and/or softening fabrics.

It may be used in a proportion of from 0.2 to 10 g/l and preferably from 2 to 10 g/l.

Along with the nanoparticles or the nanolatex of polymer (P), there may be present other constituents of the type such as:

- combinations of cationic surfactants (triethanolamine diester quaternized with dimethyl sulphate, N-methyl-imidazoline tallow ester methyl sulphate, dialkyl-dimethylammonium chloride, alkylbenzyldimethylammonium chloride, methyl alkylimidazolinium sulphate, methyl methylbis(alkylamidoethyl)-2-hydroxyethylammonium sulphate, etc.) in an amount which may range from 3% to 50% and preferably from 4% to 30% of the said formulation, optionally combined with nonionic surfactants (ethoxylated fatty alcohols, ethoxylated alkylphenols, etc.) in an amount which may be up to 3%;

- optical brighteners (0.1% to 0.2%);
- optionally, colour-fast agents (polyvinylpyrrolidone, polyvinyloxazolidone, polymethacrylamide, etc. 0.03% to 25% and preferably 0.1% to 15%),
- colorants,
- fragrances,
- solvents, in particular alcohols (methanol, ethanol, propanol, isopropanol, ethylene glycol or glycerol),
- foam limiters.

A third embodiment of the care composition of the invention consists of an additive for drying fabrics in a suitable tumble dryer.

The said additive comprises a flexible solid support consisting, for example, of a strip of woven or nonwoven textile or a sheet of cellulose, comprising nanoparticles or impregnated with the nanolatex of polymer (P); the said additive is introduced at the time of tumble-drying into the wet fabrics to be dried at a temperature from about 50 to 80°C for 10 to 60 minutes.

The said additive may also comprise cationic softeners (up to 99%) and colour-fast agents (up to 80%), such as those mentioned above.

A fourth embodiment of the care composition of the invention consists of an ironing formulation which may be sprayed directly onto the dry fabrics before ironing.

The said formulation may also contain silicone-based polymers (from 0.2% to 5%), nonionic surfactants (from 0.5% to 5%) or anionic surfactants (from 0.5% to 5%), fragrances (0.1% to 3%) or cellulose derivatives (0.1% to 3%), for instance starch; spraying the said formulation onto the fabrics makes it easier to iron them and limits the creasing of the fabrics when they are worn.

A fifth embodiment of the care composition of the invention consists of a prespotter which is in the form of an aqueous dispersion or a solid (stick).

Along with the nanoparticles or the nanolatex of polymer (P), there may be present other constituents of the type such as:

- anionic surfactants such as those already mentioned above, in an amount of at least 5% of the weight of the composition
- nonionic surfactants such as those already mentioned above, in an amount which may range from 15% to 40% of the weight of the composition
- aliphatic hydrocarbons, in an amount which can range from 5% to 20% of the weight of the composition.

A second subject of the invention consists of a process for caring for fabrics by treating them with a composition, in an aqueous or wet medium, comprising at least nanoparticles or a nanolatex of at least one polymer (P) that is insoluble in the said medium.

The type of composition, and also the amounts of polymer (P) and other additives which may be used, have already been mentioned above.

A third subject of the invention consists of the use, in a composition for treating fabrics in an aqueous or wet medium, of nanoparticles or of at least one nanolatex of at least one polymer (P) that is insoluble in the said medium, as a fabric care agent.

The type of composition, and also the amounts of polymer (P) and other additives which may be used, have already been mentioned above.

The said nanoparticles or the said nanolatex protect the fabrics in particular against physical or chemical degradation and/or give them benefits such as softening and/or crease-resistance properties.

The diameters of the nanoparticles or nanolatices of polymer according to the invention may be determined in a well-known manner by light scattering or by transmission electron microscopy.

The examples which follow are given for illustrative purposes.

The polymer (P) latices used to prepare the formulations in the examples of the invention are the latices (I) and (II) below:

Latex (I) of

* methyl methacrylate/butyl acrylate/hydroxyethyl methacrylate/methacrylic acid/N,N-dimethyl-N-meth-

acryloyloxyethyl-N-(3-sulphopropyl)ammonium sulphobetaine (SPE from Raschig)

in a mass ratio between the various monomers of

42.3/35.4/15.8/4.2/2.2

the glass transition temperature Tg of which is about 41°C

having a mean particle size from about 35 to 45 nm (determination by light scattering using a Malvern Instrument Zetasizer machine) and a solids content of about 30%.

Latex (II) of

* methyl methacrylate/butyl acrylate/hydroxyethyl methacrylate/methacrylic acid,

in a mass ratio between the various monomers of

37/55/5/3

the glass transition temperature Tg of which is about 17°C

having a mean particle size from about 30 to 35 nm (determination by light scattering using a Malvern Instrument Zetasizer machine) and a solids content of about 30%.

Example 1

Detergent formulation

Formulation	**(A) with P**	**(B) colour without P**	**(C) without P**
Constituents	**% by weight**	**% by weight**	**% by weight**
NaTPP	40		
Zeolite 4A	0	25	25
2 SiO_2, Na_2O silicate	5	5	5
Sodium carbonate	5	15	15
Acrylate/maleate copolymer Sokalan CP5 (BASF)	0	5	5
Sodium sulphate	8	21	8
CMC blanose 7MXF (Hercules)	1	1	1
Perborate monohydrate	15	0	15
Granulated TAED	5	0	5
Anionic surfactant Laurylbenzene sulphate (Nansa)	6	8	6
Nonionic surfactant Symperonic A3 (3 EO ethoxylated alcohol - ICI)	3	5	3
Nonionic surfactant Symperonic A9 (9 EO ethoxylated alcohol - ICI)	9	11	9

Formulation	(A) with P	(B) colour without P	(C) without P
Constituents	**% by weight**	**% by weight**	**% by weight**
Enzymes (esterases, amylases, cellulase, protease)	0.5	0.5	0.5
Fragrances	1	1	1
Latex (I) (% solids)	1.0	1.0	1.0
Polyvinylpyrrolidone	0	1	0
Soil-release sulphonated copolyester Repel-O-Tex PF 594 from Rhodia	0.5	0.5	0.5

A washing operation is carried out in a Tergotometer laboratory machine which is well known in the profession to detergent composition formulators. The machine simulates the mechanical and thermal effects of pulsating-type American washing machines, but, by virtue of the presence of 6 washing drums, it makes it possible to carry out simultaneous series of tests with an appreciable saving in time.

25 × 25 cm test pieces are cut from unfinished cotton. The cotton test pieces are first ironed so that they all have the same level of creasing before washing.

They are then washed using the above detergent formulation containing latex (I) and rinsed once, under the following conditions:

- number of test pieces per Tergotometer drum: 2
- volume of water: 1 litre
- water of French hardness 30°TH obtained by suitable dilution of Contrexéville® brand mineral water
- washing product concentration: 5 g/l
- washing temperature: 40°C
- washing time: 20 min
- spin speed of the Tergotometer: 100 rpm
- rinsing with cold water (about 30°TH)
- rinsing time: 5 minutes

The test pieces are then creased under a 3 kg press for 20 seconds, after which they are dried vertically overnight.

The same operation is carried out using the same detergent formulation, but free of latex (I).

A digital colour photograph is then taken of the dry test pieces, which is then converted into 256 grey scale levels (grey scale from 0 to 255).

The number of pixels corresponding to each grey scale level are counted.

For each histogram obtained, the standard deviation σ of the distribution of the grey scale level is measured.

$\sigma 1$ corresponds to the standard deviation obtained with the detergent formulation containing no latex.

$\sigma 2$ corresponds to the standard deviation obtained with the detergent formulation containing latex (I).

The performance value is given by the equation $-\Delta\sigma = \sigma 2 - \sigma 1$

The performance values obtained are as follows:

Formulation	**(A)**	**(B)**	**(C)**
$-\Delta\sigma$	3.5	4	4.5

These positive values of $-\Delta\sigma$ are representative of a crease-resistance property provided by the detergent formulation comprising the latex according to the invention.

Example 2

Rinsing/softening formulation

Constituents	**% by weight**
Cationic surfactant : ditallow dimethylammonium chloride	5%
Fragrance	1%
HCl to obtain a pH = 3	0.2%
Latex (I) or (II) (% solids)	2%